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## III.B.7 Hexaaluminate Reforming Catalyst Development

### Objectives

- The development of a durable, low-cost catalyst to reform middle distillate fuels.
- Evaluate the activity and selectivity of transition metal-doped hexaaluminate-type catalysts.
- Evaluate the effect of GDC10 (10 wt% gadolinium-doped cerium oxide) addition to the surface of hexaaluminate-type catalysts as a method of controlling carbon deposition.
- Further elucidate the effect of space velocity on carbon deposition and the presence of olefins.

### Approach

- Synthesize and characterize noble metal-doped hexaaluminate-type catalysts.
- Evaluate catalyst activity and selectivity with No. 2 diesel fuel (DF-2).
- Synthesize  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.6}$  catalysts with 1, 2 and 3 wt% GDC10 supported on the surface. Test and evaluate the effect of  $\text{O}_2$ -ion film addition on carbon deposition.

### Accomplishments

- Demonstrated 25 hours of stable operation on DF-2 at a gas hourly space velocity (GHSV, at 1 atm and 273.15 K) of  $25,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$ .
- Synthesized 20 different hexaaluminate-type catalyst formulations.
- Performed catalyst characterization by x-ray diffraction, temperature-programmed reduction and temperature-programmed oxidation (TPO).
- Evaluated the activity and selectivity of synthesized hexaaluminate samples using DF-2.

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- Evaluated the effect of adding 1, 2 and 3 wt% GDC10 to the surface of  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.6}$  on the formation of carbon.
- Evaluated the effect of GHSV on catalyst selectivity and the formation of olefin compounds and carbon deposition.

### Future Directions

- Improved catalyst activity:
  - Evaluate activity and selectivity of platinum group metal-doped hexaaluminate catalysts.
- Improved carbon formation resistance:
  - Continue to evaluate the effect of  $\text{O}_2$ -ion conducting surface treatments and the use of  $\text{O}_2$ -ion conducting bed packing materials.
- Improved sulfur resistance:
  - Evaluate the effects of high temperature operation on sulfur resistance.

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### Introduction

Reforming middle distillate fuels for distributed fuel cell power is a very attractive source of  $\text{H}_2$  and CO. However, these fuels contain heavy hydrocarbons that are prone to coking and contain organosulfur compounds which are not easily removed. The simplest reforming technology employs a catalyst to reform the fuel into  $\text{H}_2$  and CO and to convert the organosulfur compounds into more easily removed  $\text{H}_2\text{S}$ . This approach necessitates the development of a catalyst which does not deactivate under these conditions.

For this application, the National Energy Technology Laboratory (NETL) is developing a new class of catalysts based on transition metal-doped hexaalumina. The use of hexaalumina is of growing importance in catalysis due to its refractory nature [1,2]. The thermal stability of hexaalumina is attributed to its structure, which has proven useful in retaining the large surface area necessary for catalytic reaction [2]. In this project, catalytically active metals are doped directly into the hexaalumina lattice resulting in an atomically dispersed catalyst system that has been shown to possess carbon deposition resistance [3,4].

### Approach

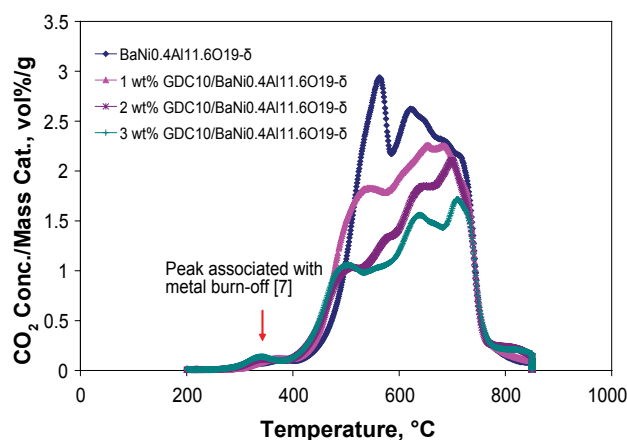
At high temperatures, carbon deposition onto the surface of a reforming catalyst occurs predominately through pyrolytic and dehydrogenation reactions. The

selectivity of hydrocarbons toward dehydrogenation into coke occurs when hydrocarbons are adsorbed strongly to the surface of the catalyst [5, 6]. It is, therefore, desirable to design catalyst systems which limit strong hydrocarbon adsorption tendencies and reduce the residence time of the hydrocarbon intermediates on the surface of the catalyst.

The aim of the present study has been to minimize the formation of large ensembles of active sites that are responsible for strongly adsorbing hydrocarbons and sulfur compounds onto the surface of a catalyst. The approach examined here was to substitute catalytically active metals into the framework lattice of a solid oxide. For this application hexaalumina was selected due to its refractory properties. A series of catalysts based on transition metal-doped hexaalumina were prepared by co-precipitation from nitrate salt precursors. The stability of one of the catalysts was assessed over 25 hours of continuous operation on DF-2. Catalyst activity and selectivity were investigated as a function of GHSV. The carbon deposition resistance of  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.8}$  treated with 1, 2 and 3 wt% GDC10 was also evaluated.

## Results

The effect of adding  $\text{O}_2$ -ion conducting films to the surface of hexaaluminate catalysts was evaluated as a potential method to mitigate carbon deposition. GDC10 films of 1, 2 and 3 wt% were applied to the surface of a  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.8}$  reforming catalyst. The effect of carbon deposition was evaluated by reforming n-tetradecane for 5 hours over the catalysts at a GHSV =  $50,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$ , an O/C = 1.2, a T =  $850^\circ\text{C}$  and a P = 2 atm followed by TPO of the carbon deposits. The TPO results are given in Figure 1. From this figure, a low temperature burn-off peak centered at  $350^\circ\text{C}$  was observed for all catalysts. This peak is associated with carbon deposited onto the catalytically active metal



**FIGURE 1.** The Effect of 1, 2 and 3 wt% GDC10 Addition to  $\text{BaNi}_{0.4}\text{Al}_{11.6}\text{O}_{19.8}$  on Carbon Deposition

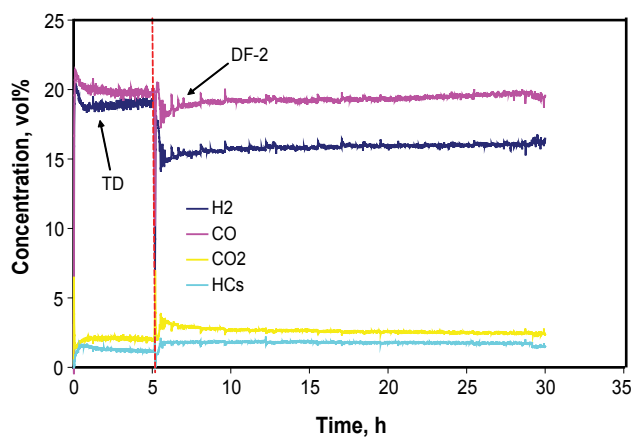
site [7]. Higher temperature carbon burn-off was also observed for all four catalysts. Carbon burn-off at higher temperatures is associated with carbon deposited onto the catalyst support. From this figure it is observed that as the GDC10 concentration is increased, the amount of carbon deposited onto the surface of the catalyst was reduced. This indicates that the addition of  $\text{O}_2$ -ion conducting materials to hexaaluminate catalysts may be an effective approach to reduce carbon deposited onto the catalyst surface.

The partial oxidation performance of a noble metal doped hexaaluminate-type catalyst (HEXM-1) was evaluated by the partial oxidation of DF-2. The catalytic performance of HEXM-1 catalyst is given in Figure 2. The composition of the DF-2 fuel tested is given in Table 1. The reaction conditions investigated were a GHSV =  $25,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$ , an O/C = 1.2, a total inlet flow rate of 450 sccm (with 50 sccm  $\text{N}_2$  diluent) a fuel pre-heat temperature of  $350^\circ\text{C}$ , T =  $900^\circ\text{C}$  and P = 2 atm.

**TABLE 1.** DF-2 Composition

Constituent	Concentration (wt%)
Sulfur	9 ppmw
Aromatic	18
Paraffin	38
Naphthenes	44

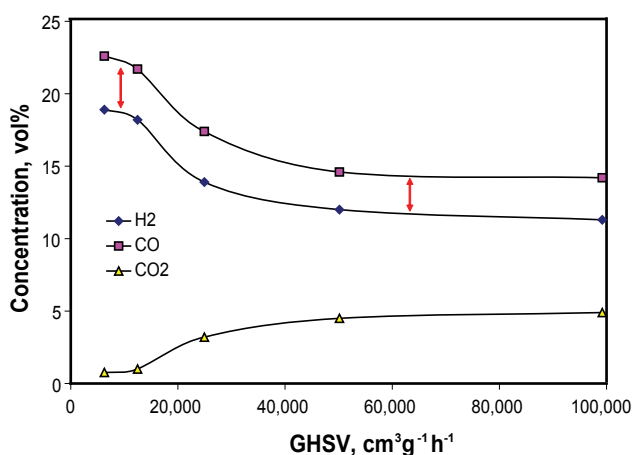
The first 5 hours of the run were performed on n-tetradecane (TD) to condition the catalyst and baseline catalytic performance. During this time period the catalyst exhibited some changes in selectivity and  $\text{CO}$  and  $\text{H}_2$  yields. The hydrocarbon feed was then switched to DF-2 which resulted in an immediate change in selectivity as well as  $\text{H}_2$  and  $\text{CO}$  yields. This change in catalyst performance is attributed to strongly adsorbing, less reactive feed constituents present in the DF-2.



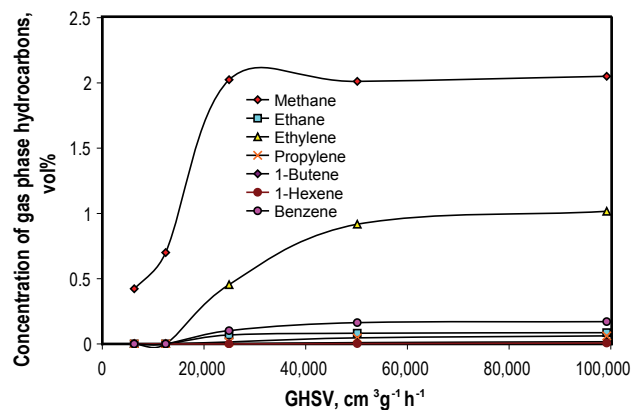
**FIGURE 2.** The Partial Oxidation of DF-2 over HEXM-1 Catalyst; GHSV =  $25,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$ , T =  $900^\circ\text{C}$ , P = 2 atm, O/C = 1.2

CO<sub>2</sub> and hydrocarbon slip concentrations increased only marginally indicating that catalytic reactions were occurring predominately over gas phase reactions. The catalyst was then run for another 25 hours on DF-2 where it exhibited stable performance.

Also examined was the effect of varying the catalyst space velocity on the partial oxidation performance of HEXM-1 with DF-2. In this study, the O/C = 1.2 was kept constant with a total inlet flow rate of 450 sccm (with 50 sccm N<sub>2</sub> diluent), a fuel pre-heat temperature of 350°C was utilized, the temperature was kept isothermal at T = 900°C and the pressure was kept constant at P = 2 atm. The space velocity of the reactor was varied from 6,250 to 100,000 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>. The data points were taken after 2 hours into the experimental run. From Figure 3 it is observed that as space velocity is increased, the H<sub>2</sub> and CO concentrations both decreased. With the



**FIGURE 3.** The Partial Oxidation of DF-2 over HEXM-1 Catalyst; Effect of Space Velocity on Catalyst Activity; T = 900°C, P = 2 atm, O/C = 1.2



**FIGURE 4.** The Partial Oxidation of DF-2 over HEXM-1 Catalyst; Effect of Space Velocity on Hydrocarbon Slip; T = 900°C, P = 2 atm, O/C = 1.2

steepest decrease in H<sub>2</sub> and CO concentration occurring as GHSV was increased from 12,500 and 25,000 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>. Correspondingly, CO<sub>2</sub> concentration increased with GHSV indicating that gas phase chemistry was also increasing.

From Figure 4, increasing the space velocity also increased the hydrocarbon slip through the catalytic bed. Both methane and ethane concentrations were observed as sharply increasing from 6,250 to 25,000 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>. Benzene and residual olefins became observable at space velocities in excess of 12,500 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>.

## Conclusions

The carbon deposition resistance of a BaNi<sub>0.4</sub>Al<sub>11.6</sub>O<sub>19.8</sub> catalyst treated with 1, 2 and 3 wt% GDC10 films was examined. Carbon deposition onto the catalyst surface was shown to decrease with increasing concentration of the GDC10 film. A series of catalysts based on noble metal doped onto hexaalumina were also synthesized. One of the catalysts exhibited excellent stability over 25 hours of continuous operation on DF-2. The activity and selectivity of this catalyst were examined over a range of space velocities. At space velocities exceeding 12,500 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup> gas phase reaction became more pervasive as well as hydrocarbon slip.

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## FY 2006 Publications/Presentations

1. "Effect of Nickel Hexaaluminate Mirror Cation on Structure Sensitive Reactions during n-Tetradecane Partial Oxidation," Submitted to Applied Catal., Gardner, T. H.
2. "Hexaaluminate Catalysts for the Partial Oxidation of Middle Distillate Fuels," ACS Spring Meeting, Atlanta, GA, 2006, Gardner, T. H., Shekhawat, D., Berry, D. A.